Instrumental Analysis and Quantitation of Polycyclic Aromatic Hydrocarbons and Atrazine:

IADN Project

Donald Cortes and Wayne Brubaker
School of Public and Environmental Affairs
Indiana University
Bloomington, IN 47405

July 1996

Version 1.3

Instrumental Analysis and Quantitation of Polycyclic Aromatic Hydrocarbons and Atrazine: IADN Project

1.0 Introduction

This document briefly outlines the instrumental analysis and quantitation of polycyclic aromatic hydrocarbons (PAH) and atrazine collected in air and precipitation samples from three sites on the Great Lakes. This work is conducted at the School of Public and Environmental Affairs, Indiana University-Bloomington as a part of the Integrated Atmospheric Deposition Network (IADN). The following summarizes the gas chromatographic-mass spectrometry (GC-MS) technique used, its pertinent parameters, and analyte quantitation.

PAH analyses are performed on a Hewlett-Packard (HP) 5890 Series II gas chromatograph and a HP 5989 mass spectrometer. Chromatographic resolution is achieved with a 30 m × 250 µm DB-5 capillary column which has a 0.25 µm film thickness (J & W Scientific, Folsom, CA) with helium carrier gas. PAHs are quantified by GC-MS using selected ion monitoring (SIM) and the method of internal standards. The PAHs analyzed in this study are listed in Table 1 along with the primary and secondary ions from their mass spectra.

Table 1. Target compounds and their monitored ions.

Retention Order	Compound	Major Ion	Secondary Ion
1	d10-anthracene*	188	----
2	acenaphthylene	152	151
3	acenaphthene	153	154
4	fluorene	166	165
5	d10-phenanthrene**	188	----
6	phenanthrene	178	176
7	anthracene	178	176
8	fluoranthene	202	101
9	pyrene	202	101
10	retene	219	234
11	d12-benzo (a) anthracene*	240	----
12	benzo (a) anthracene	228	114
13	chrysene	228	114
14	d12-perylene*	264	---
15	benzo (b) fluoranthene	252	126
16	benzo (k) fluoranthene	252	126
17	benzo (e) pyrene	252	126
18	benzo (a) pyrene	252	126
19	indeno (1,2,3,cd) pyrene	276	138

Table 1. Target compounds and their monitored ions.

Retention Order	Compound	Major Ion	Secondary Ion
20	dibenzo (a,h) anthracene	278	139
21	benzo (g,h,i) perylene	276	138
22	coronene	300	150

*internal standard
**surrogate standard

2.0 Performance Evaluation

Prior to analyzing a sample set, the GC-MS system performance and calibration are verified for all analytes. The mass spectrometer is tuned immediately before the running of a sample batch using the system's operating software programs (AUTOTUNE) with perfluorotributylamine (PFTBA) calibration gas. Mass spectrometer parameters are adjusted so that masses 69, 219, and 502 and their respective isotopes meet the target mass-intensity criteria. A sample AUTOTUNE report is included.

Hexane is injected prior to the running of a sample set to insure the system is free from contaminants or interfering peaks. The Relative Percent Difference (RPD) between a calibration standard and a performance standard should be withing 20%.

Sample injections and system maintenance are recorded in the appropriate laboratory logbooks located near the instrument.

3.0 Instrumental Parameters

The GC oven temperature program is given in Table 2. Other significant gas chromatographic parameters are:

Carrier gas:	helium (99.999%; Liquid Carbonic, Chicago)
Injector:	On Column, Constant Flow
Injection volume:	1 µL
Transfer line:	300°C

The mass spectrometer is operated in the electron ionization (EI) mode with ion source and quadrapole temperatures of 250°C and 100°C respectively.

Table 2. GC oven temperature program for PAH analysis

Initial Temperature: 40°C

Initial Time: 3.00 min

Rate (°C/min)	Final Temperature (°C)	Final Hold Time (min)
30.0	240	0.00
50.0	300	11.7

Total Run Time: 22.70 min

4.0 Sample Analysis

The extracted samples, lab blanks and matrix spikes are stored in 4-mL amber vials at -20°C until they are ready for analysis. They contain approximately 1 mL of solvent (hexane) and were previously spiked with 50 µL of the internal standard solution (see Table 3).

Table 3. Internal standard solution.

Compound	Concentration (ng/µL)
d10-anthracene	4.00
d12-benzo(a)anthracene	4.00
d12-perylene	4.00

Standards and samples are brought to room temperature before they are injected. After the hexane blank is injected, a calibration standard (see Table 5) is injected followed by the samples. All injections are performed manually with 1 µL volumes.

The mass spectrometer is turned on after a four minute solvent delay. Data is acquired in selected ion mode. Windows and ion ranges are given in Table 6.

5.0 Data Reduction and Analyte Quantitation

Data is collected and stored within the system's HP Apollo 400 computer. Mass chromatograms are generated, and their peaks are integrated with the accompanying software programs. Chemstation Enviroquant prepares quantitation reports with individual mass chromatograms and spectra for all target analytes.

For each day of samples run, relative response factors (RRFs) for each analyte are determined from the calibration standard's peak areas using Equation 1.

$$RRF_{std} = \left(\frac{mass_a}{area_a} \right)_{std} \div \left(\frac{mass_{istd}}{area_{istd}} \right)_{std}$$

Where $mass_a$ *= the analyte's known mass in the injected amount of calibration standard,*
$area_a$ *= the analyte's peak area,*
$mass_{istd}$ *= the known mass of the appropriate internal standard, and*
$area_{istd}$ *= that internal standard's peak area.*

With reference to Table 1, the response factors for compounds 2-10, 12-13, and 15-22 are calculated relative to the internal standards d10-anthracene, d12-benzo(a)anthracene, and d12-perylene respectively.

An analyte's mass in a sample ($mass_a$) is calculated from the RRF_{std} above and the internal standard response in the sample by the following equation:

$$(mass_a)_{sample} = (area_a)_{sample} \; x \; RRF_{std} \; x \left(\frac{mass_{istd}}{area_{istd}} \right)_{sample}$$

Where $area_a$ *= the analyte's peak area in the sample,*
$mass_{istd}$ *= the mass of internal standard spiked into the sample, and*
$area_{istd}$ *= the internal standard's peak area in the sample.*

The analyte concentrations are tabulated by Enviroquant and transferred to an Excel spreadsheet.

6.0 Quality Assurance

Each daily analytical batch includes at least one calibration standard, one performance standard, one instrument blank, one procedure blank, and one matrix spike. Acceptance criteria are summarized on the attached Table 3-1. Refer to the IADN Quality Assurance Project Plan (QAPjP) for more details.

7.0 Atrazine

Atrazine is analyzed by GC/MS in the selected ion monitoring mode. The GC temperature program is given in Table 4 below. The calibration standard contains both atrazine and the internal standard d10-anthracene at concentrations of 0.4 ng/µL.

The mass spectrometer is turned on after a solvent delay of 8.5 minutes. The ions monitored are m/z 186, m/z 188, m/z 200, and m/z 215. The ions m/z 188 and m/z 200 are the quantitation ions for d10-anthracene and atrazine respectively, and the other two are for confirmation purposes.

Table 4. GC oven temperature program for atrazine analysis.

Initial Temperature: 40°C

Initial Time: 1.00 min

Rate (°C/min)	Final Temperature (°C)	Final Hold Time (min)
25.0	140	0.00
4.0	240	0.00
20.0	290	5.00

Total Run Time: 29.50 min

8.0 Chromatograms

Mass chromatograms from a typical 1 µL injection of calibration standard are given on the following pages in Figures 1a-i. The windows on the left-hand side of each page show the quantitation peak(s) for one or more PAHs, and those on the right give the corresponding confirmation peaks. Similar mass chromatograms (Figure 2) are given for a 1 µL injection of the atrazine calibration standard.

Table 5. Calibration standard.

Retention Order	Compound	Concentration (ng/µL)
1	d10-anthracene*	0.20
2	acenaphthylene	0.20
3	acenaphthene	0.20
4	fluorene	0.20
5	phenanthrene	0.20
6	d10-phenanthrene**	0.20
7	anthracene	0.20
8	fluoranthene	0.20
9	pyrene	0.20
10	retene	0.20
11	d12-benzo (a) anthracene*	0.20
12	benzo (a) anthracene	0.20
13	chrysene	0.20
14	d12-perylene*	0.20
15	benzo (b) fluoranthene	0.20
16	benzo (k) fluoranthene	0.20
17	benzo (e) pyrene	0.19
18	benzo (a) pyrene	0.20
19	indeno (1,2,3,cd) pyrene	0.20
20	dibeno (a,h) anthracene	0.20
21	benzo (g,h,i) perylene	0.20
22	coronene	0.20

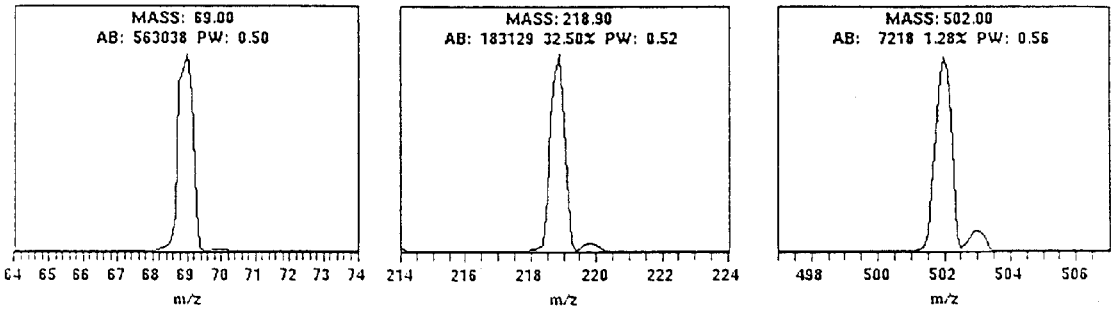
*internal standard
**surrogate standard

Table 6. SIM windows for analyte detection.

SIM Window	Start Time (min)	SIM Mass (m/z)
1	6.50	76, 83, 151, 152, 153, 154, 165, 166
2	9.80	101, 202, 176, 178, 188, 204, 219, 234
3	11.70	114, 126, 152, 228, 240, 264
4	14.80	138, 139, 150, 276, 278, 279, 300

Auto Tune
Tune File: atune.u Tue Apr 11 95 05:08:05 PM
Instrument Name: hp1 Instrument Type: 5989 Ionization Mode: EI

Repeller	7.00	Multiplier	1583	Emission	300	Integration	50
Ion Focus Gain	255	AMU Gain	167	Elec. Energy	70	Samples	16
Ion Focus	34	AMU Offset	106	Polarity	POSITIVE	Averages	1
Entrance Lens	145	Axis gain	63	Source Temp	250	Stepsize	0.12
X Ray	40	Axis Offset	4	Quad. Temp	100		



MASS	Abundance	Rel. Abund.	Iso. Mass	Iso. Abund.	Iso. Ratio
69.00	422528	100.00	70.00	4093	0.97
218.90	158464	37.50	219.90	6279	3.96
501.95	6714	1.59	502.95	672	10.01

Scan: 10.00 - 800.00 samples: 16 thresh: 20 Tue Apr 11 95 05:08:16 PM
259 peaks Base: 69.00 Abundance: 422528

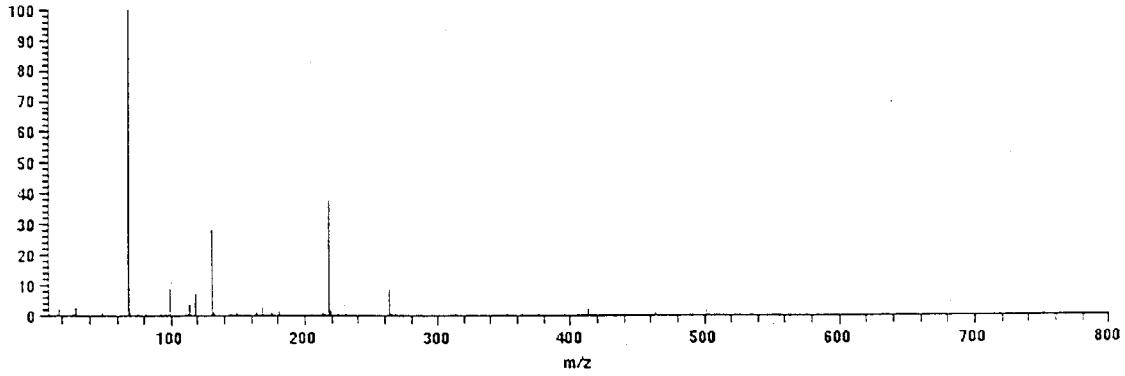
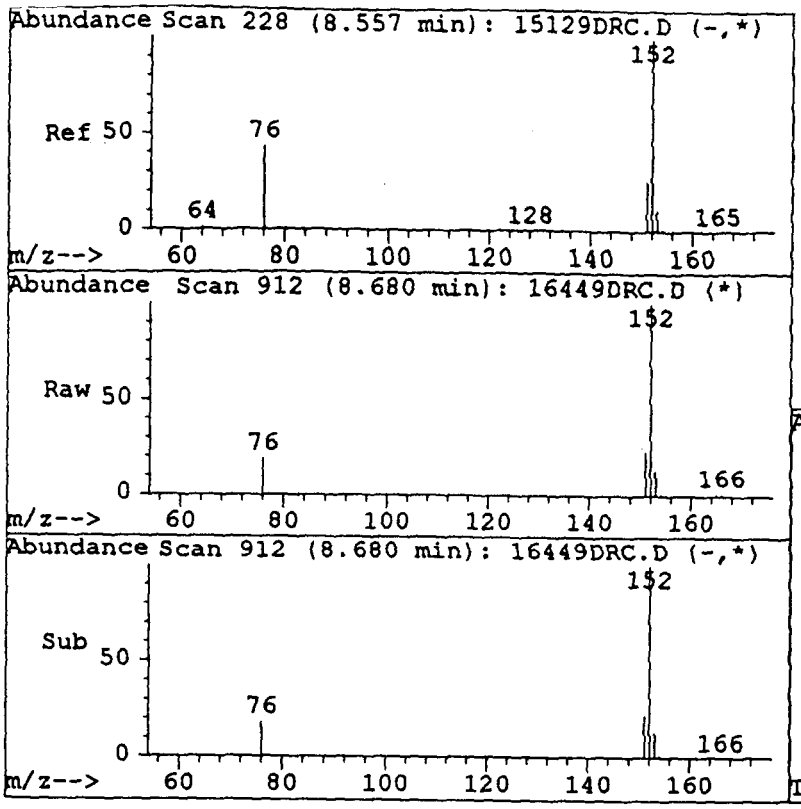


Table 3.1. Data Quality Objectives for Trace Organic Compounds

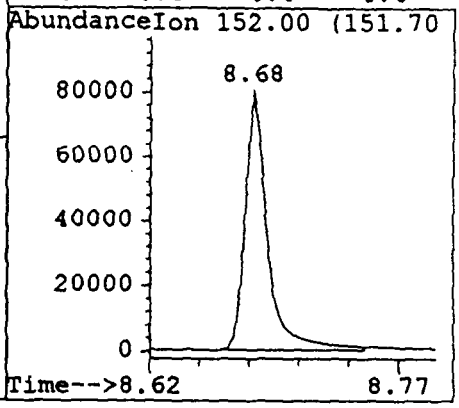
QA Criteria	QC Code	Sample Type	Frequency	Required Objective	Control Action	Units
precision	FD1/ FD2	field; co-located samplers	20%	at <5xMDL, rsd <100% at <5xMDL, rsd <50%	re-analyze if sample available; otherwise flag samples FFD or PTS	%
	LD1/ LD2	laboratory: replicate analyses	10%	at <5xMDL, rsd <50% at <5xMDL, rsd <30%	re-analyze same or alt sample; otherwise flag samples FDL or PTS	%
accuracy	LSS	surrogate spikes	all samples	50% < R <130%	flag PCB congener range FSS; investigate sources of loss	%
	LMS	matrix spikes	1/batch	50% < R < 130% for 70% of individual congeners and for average	flag sample FMS; investigate sources of loss	%
blanks	FRB	field matrix blank	10% (1/month)	<20% of associated sample mass	flag samples FFR; find source of contamination	mass
	LRB	lab matrix blank	10%	<MDL	run 2nd LRB; elminate source of imprecision; flag sample FBS	mass
completeness		field samples		90%	no action; % reported	
calibration	CLM	multiple point calibration; 4 point	annual	r^2 >0.95	reoptimize instrument, repeat calibration	
	CLS	single calibration std	1/10 samples	PCBs ± 10% actual mass	reoptimize instrument, repeat calibration	
	LPC	performance std	daily	see Table 3.2	regenerate response factors	
	LCB	lab calibration blank	2/GC run	< MDL	check for contamination; reoptimize instrument	
PCB identification		GCMS confirmation	5%			
detection limits		MDL study	1/project		reported in yearly QA Report	
detectability	RFS	routine field samples	all samples	> MDL	flag BDL	
holding time	RFS	routine field sample	all samples	1 year	flag EHT	

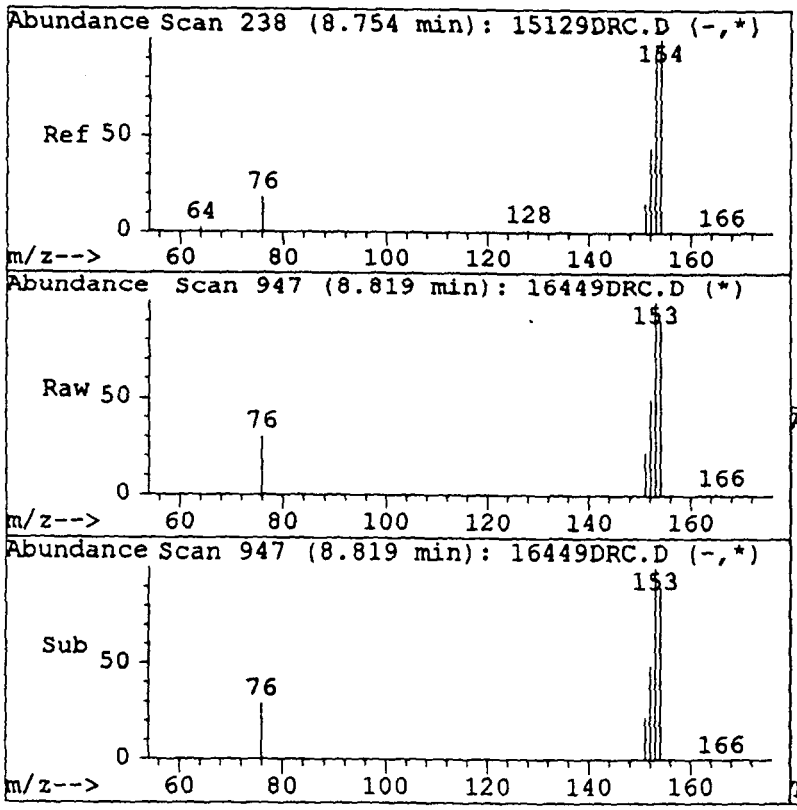


#2
Acenaphthylene
Concen: 374.36 ng
RT: 8.68 min Scan# 912
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:152 Resp: 75932

Ion	Ratio	Lower	Upper
152	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#3
Acenaphthene
Concen: 359.10 ng
RT: 8.82 min Scan# 947
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:153 Resp: 64434

Ion	Ratio	Lower	Upper
153	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

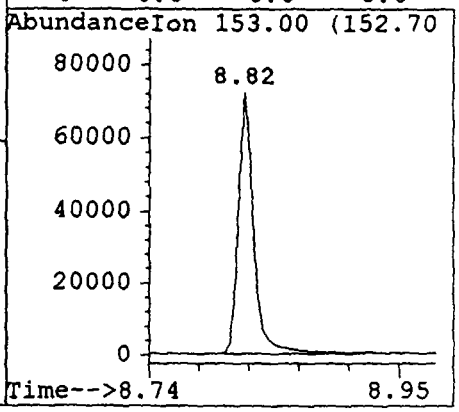
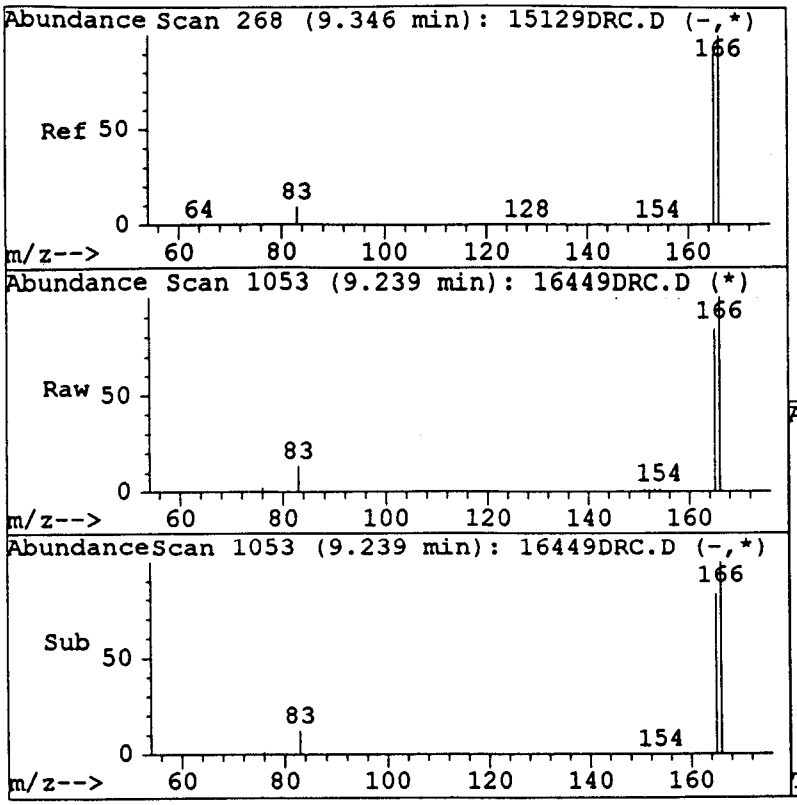


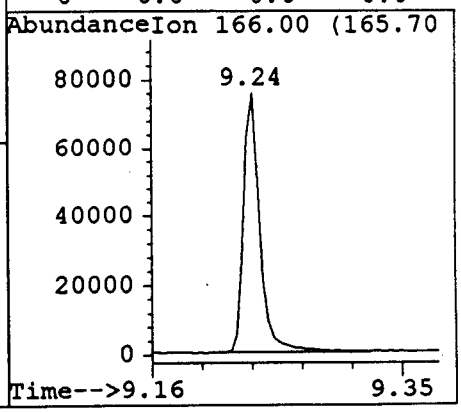
Figure 1a.

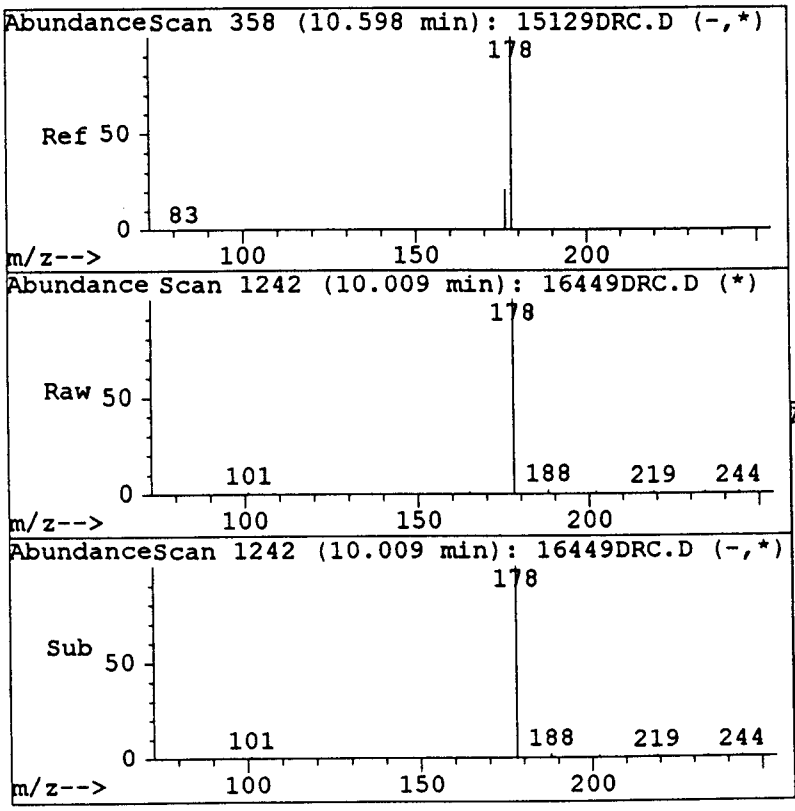


#4
Fluorene
Concen: 359.90 ng
RT: 9.24 min Scan# 1053
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:166 Resp: 64595

Ion	Ratio	Lower	Upper
166	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#6
Phenanthrene
Concen: 349.43 ng
RT: 10.01 min Scan# 1242
Delta R.T. 0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:178 Resp: 87788

Ion	Ratio	Lower	Upper
178	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

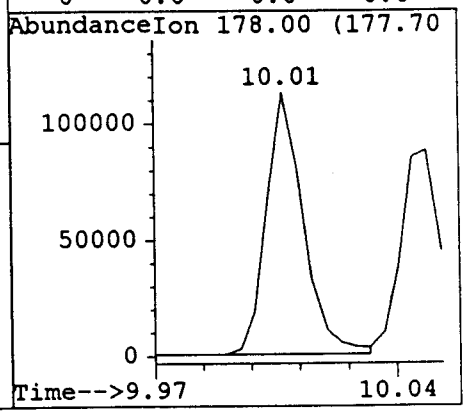


Figure 1b.

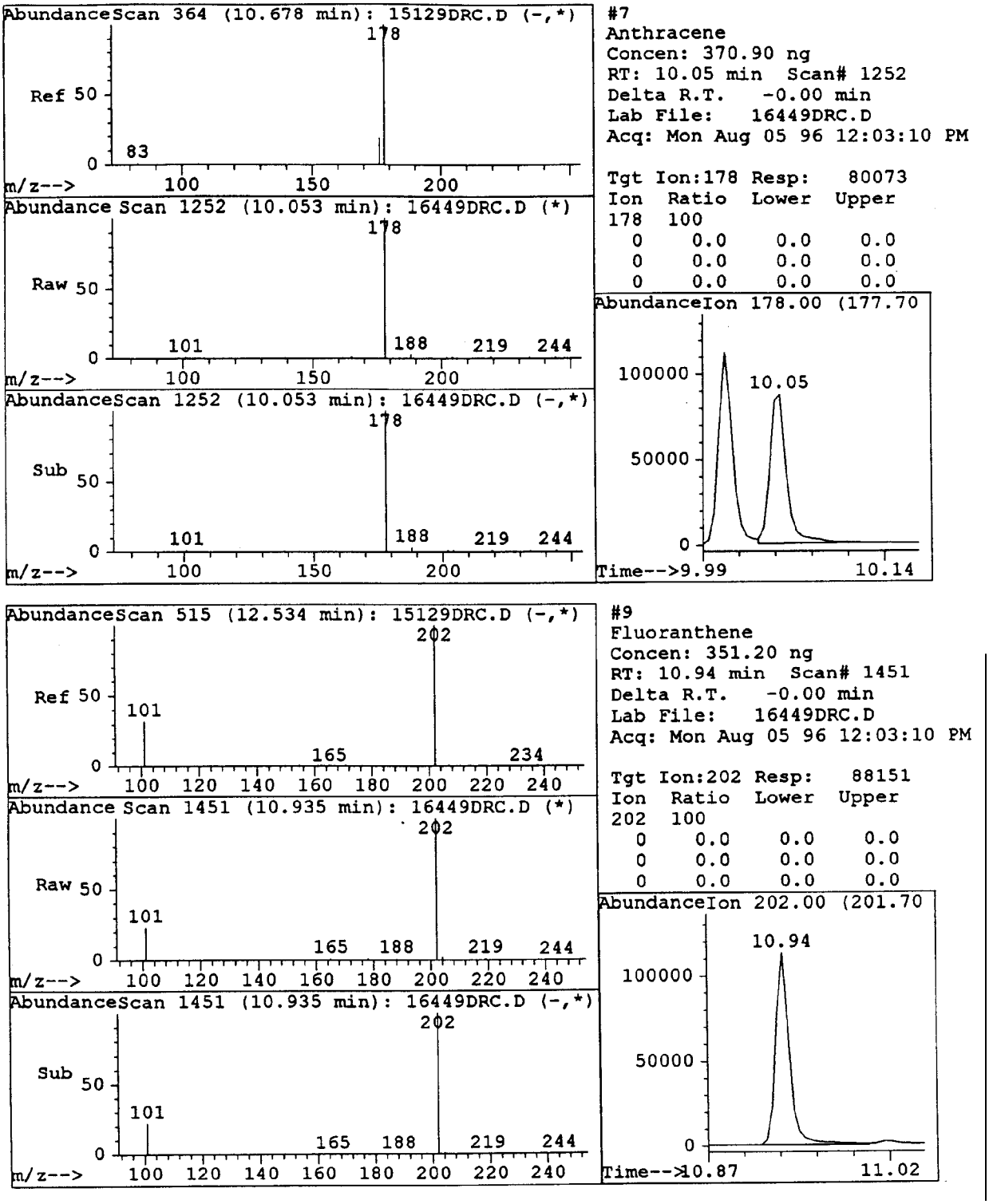
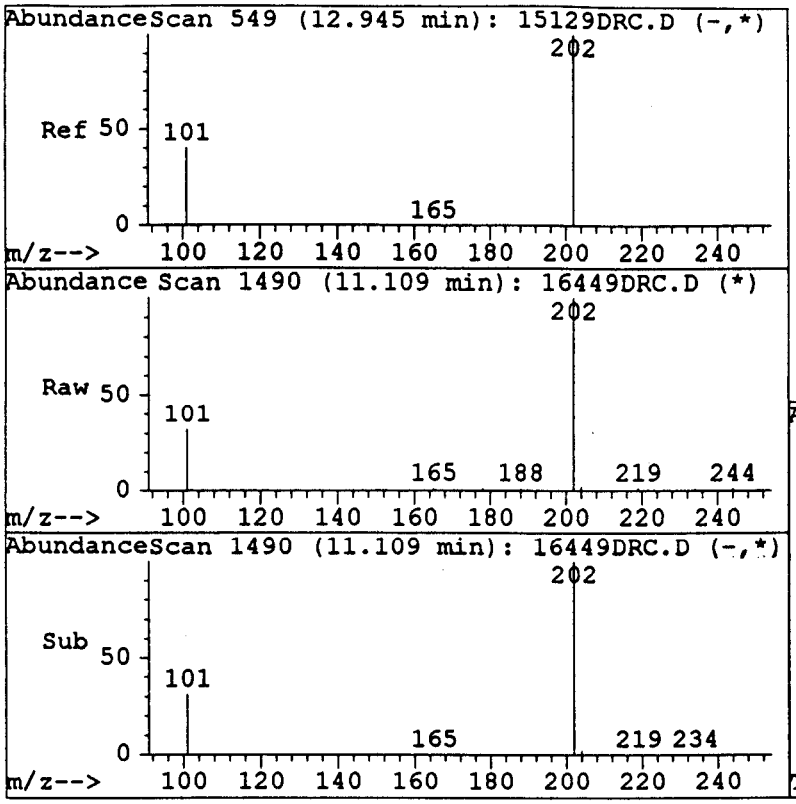

AbundanceScan 364 (10.678 min): 15129DRC.D (-,*)
Ref
178
83
Abundance Scan 1252 (10.053 min): 16449DRC.D (*)
Raw
178
101
188
219
244
AbundanceScan 1252 (10.053 min): 16449DRC.D (-,*)
Sub
178
101
188
219
244
m/z-->
100
150
200
#7
Anthracene
Concen: 370.90 ng
RT: 10.05 min Scan# 1252
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM
Tgt Ion:178 Resp: 80073
Ion Ratio Lower Upper
178 100
0 0.0 0.0 0.0
0 0.0 0.0 0.0
0 0.0 0.0 0.0
AbundanceIon 178.00 (177.70
100000
50000
0
10.05
Time-->9.99
10.14
AbundanceScan 515 (12.534 min): 15129DRC.D (-,*)
Ref
202
101
165
234
Abundance Scan 1451 (10.935 min): 16449DRC.D (*)
Raw
202
101
165
188
219
244
AbundanceScan 1451 (10.935 min): 16449DRC.D (-,*)
Sub
202
101
165
188
219
244
m/z-->
100
120
140
160
180
200
220
240
#9
Fluoranthene
Concen: 351.20 ng
RT: 10.94 min Scan# 1451
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM
Tgt Ion:202 Resp: 88151
Ion Ratio Lower Upper
202 100
0 0.0 0.0 0.0
0 0.0 0.0 0.0
0 0.0 0.0 0.0
AbundanceIon 202.00 (201.70
100000
50000
0
10.94
Time-->10.87
11.02

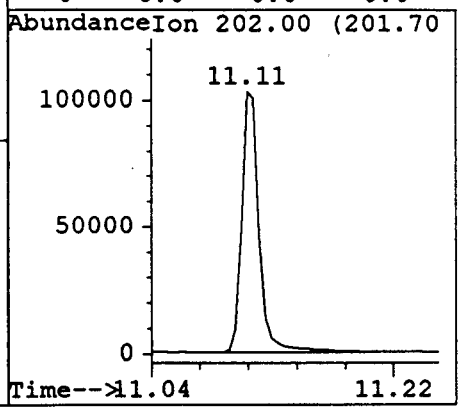
Figure 1c.

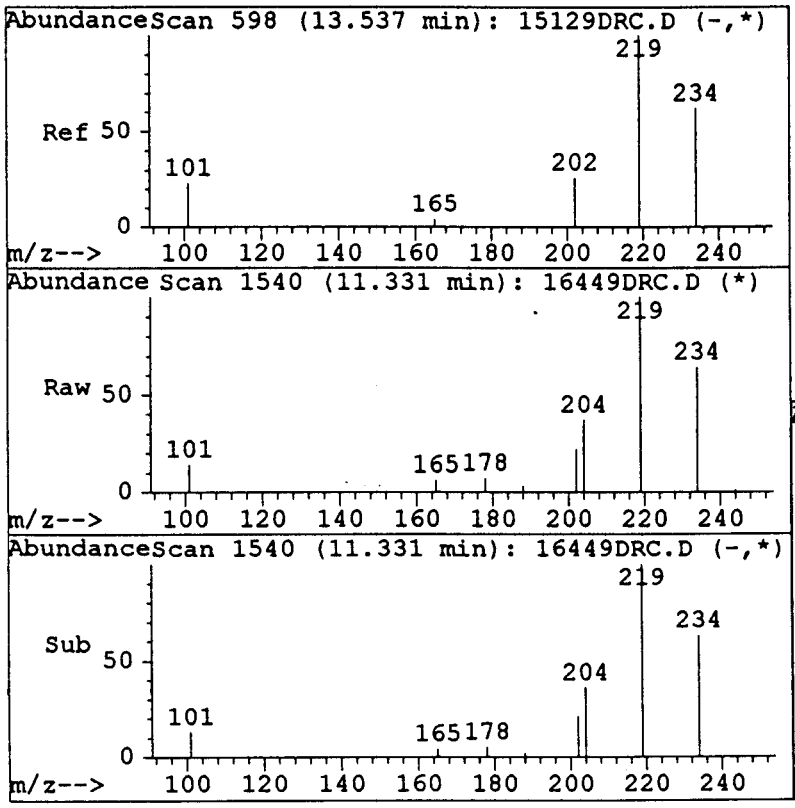


#10
Pyrene
Concen: 350.53 ng
RT: 11.11 min Scan# 1490
Delta R.T. -0.01 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:202 Resp: 91556

Ion	Ratio	Lower	Upper
202	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#11
Retene
Concen: 389.34 ng
RT: 11.33 min Scan# 1540
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:219 Resp: 33832

Ion	Ratio	Lower	Upper
219	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

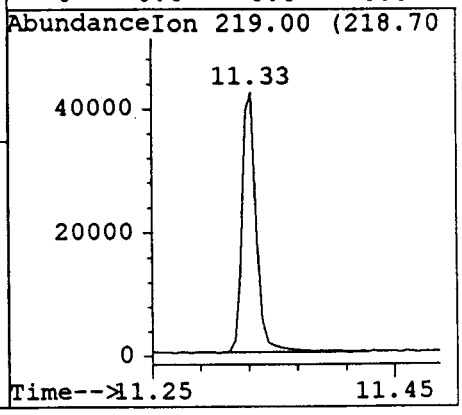
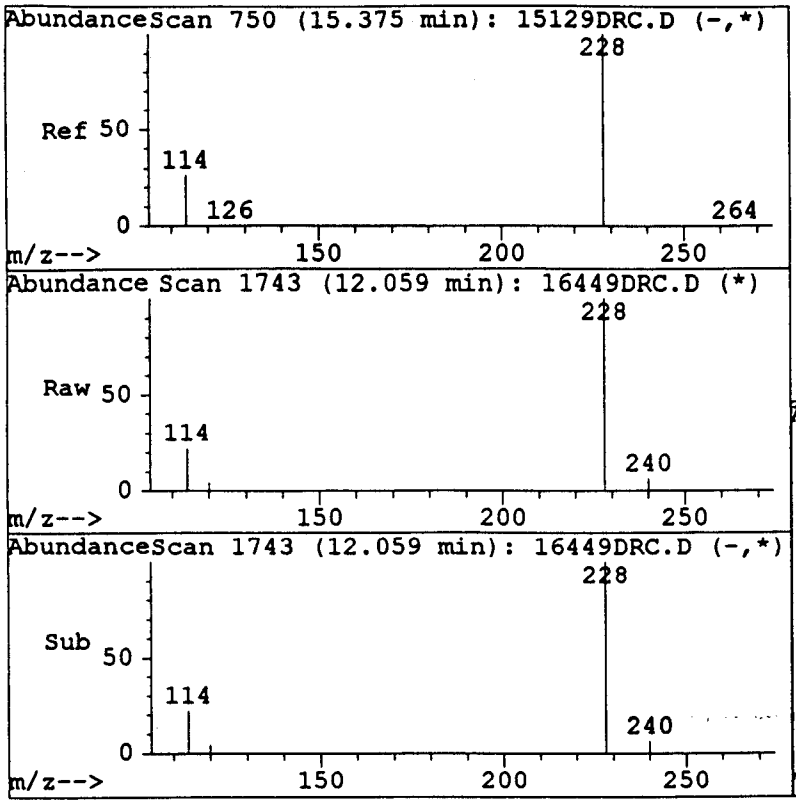


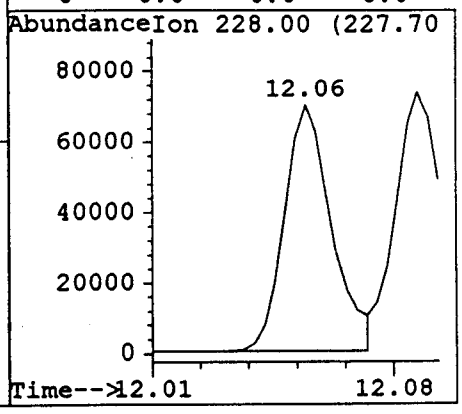
Figure 1d.

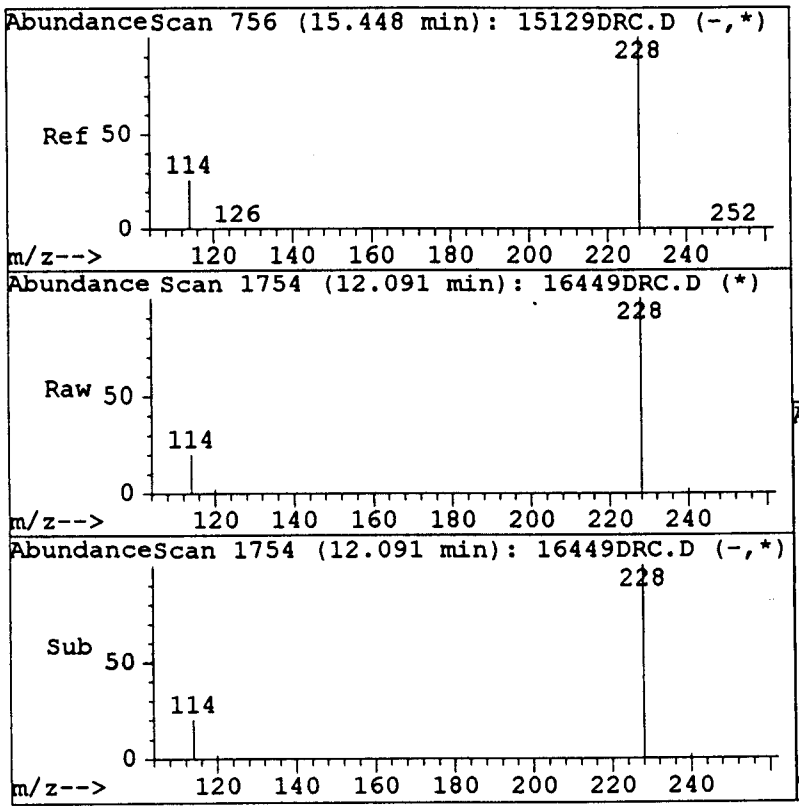


#13
Benzo(a)anthracene
Concen: 351.22 ng
RT: 12.06 min Scan# 1743
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:228 Resp: 66629

Ion	Ratio	Lower	Upper
228	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#14
Chrysene
Concen: 335.06 ng
RT: 12.09 min Scan# 1754
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:228 Resp: 80895

Ion	Ratio	Lower	Upper
228	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

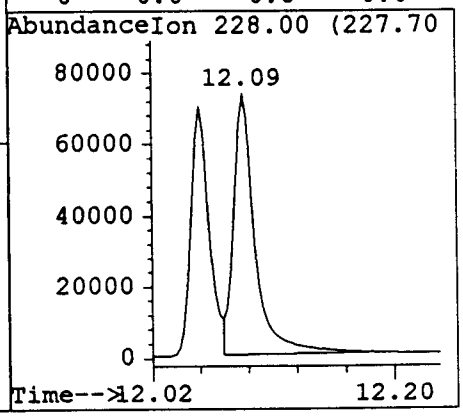
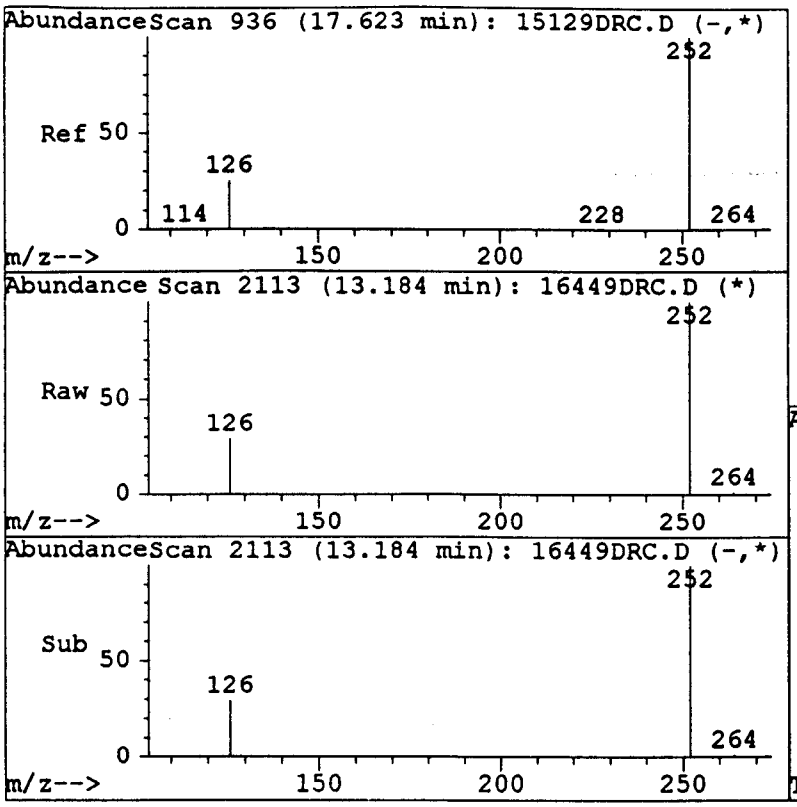


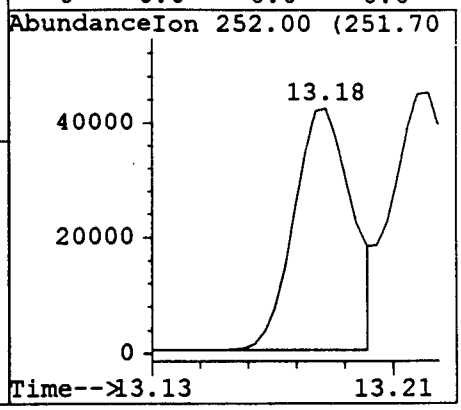
Figure 1e.

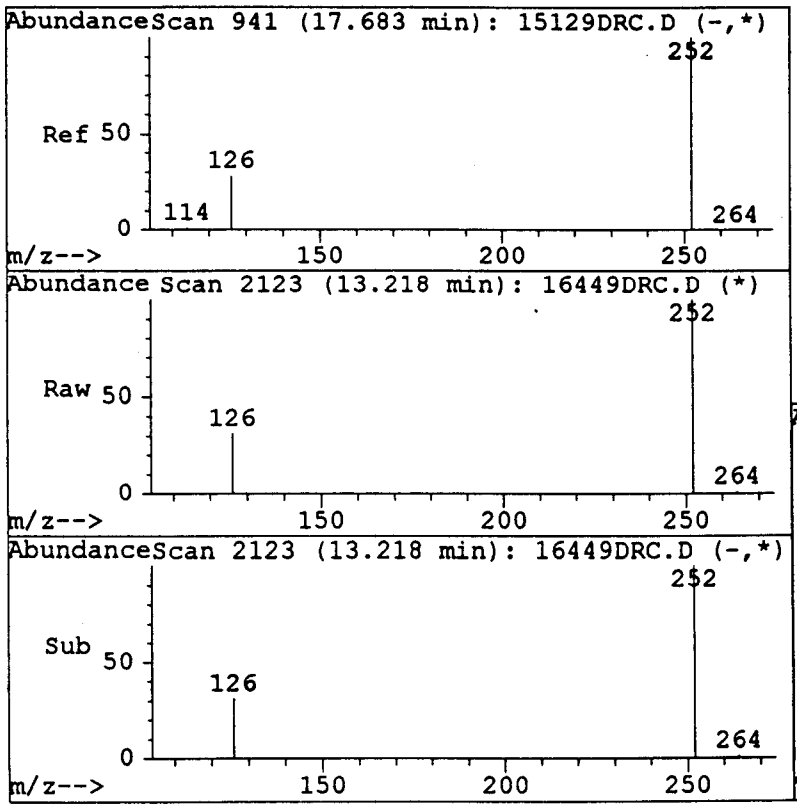


#16
Benzo(b)fluoranthene
Concen: 329.91 ng
RT: 13.18 min Scan# 2113
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:252 Resp: 55725

Ion	Ratio	Lower	Upper
252	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#17
Benzo(k)fluoranthene
Concen: 371.03 ng
RT: 13.22 min Scan# 2123
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:252 Resp: 78719

Ion	Ratio	Lower	Upper
252	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

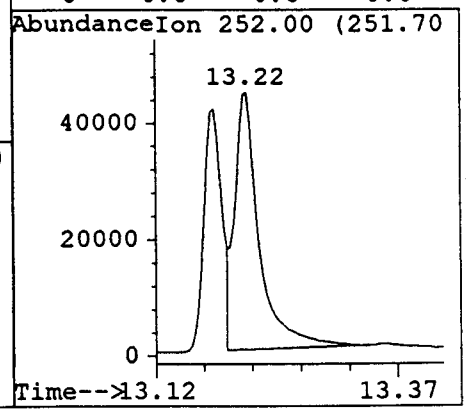
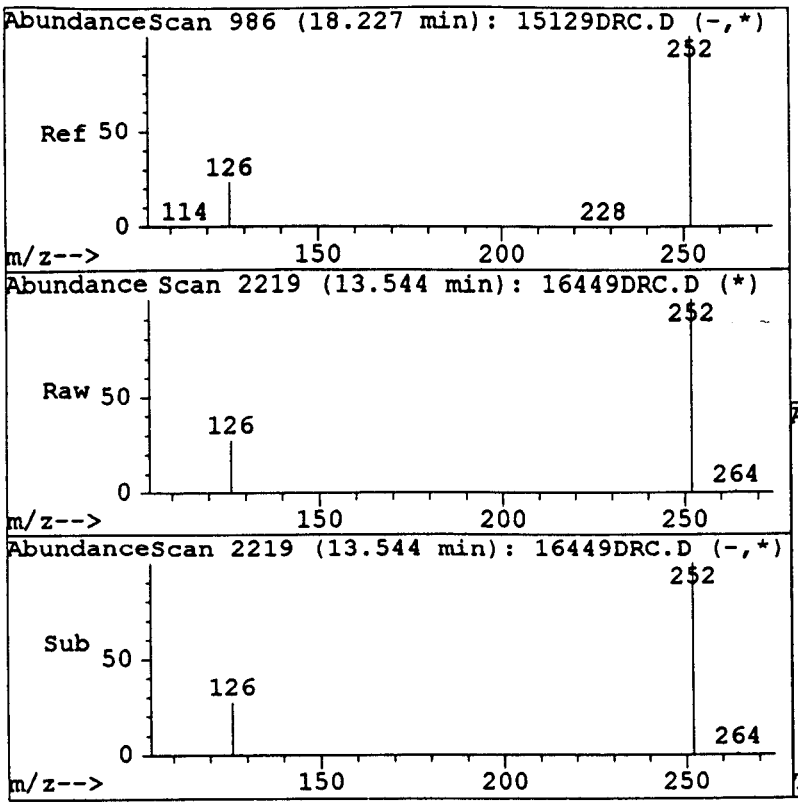


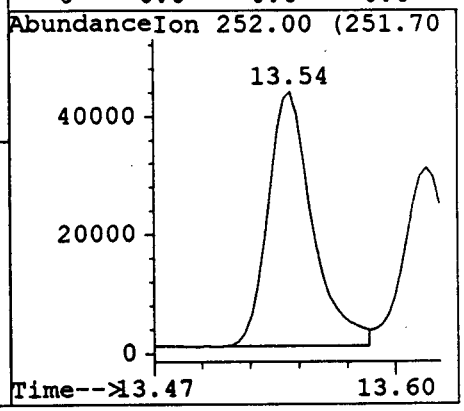
Figure 1f.

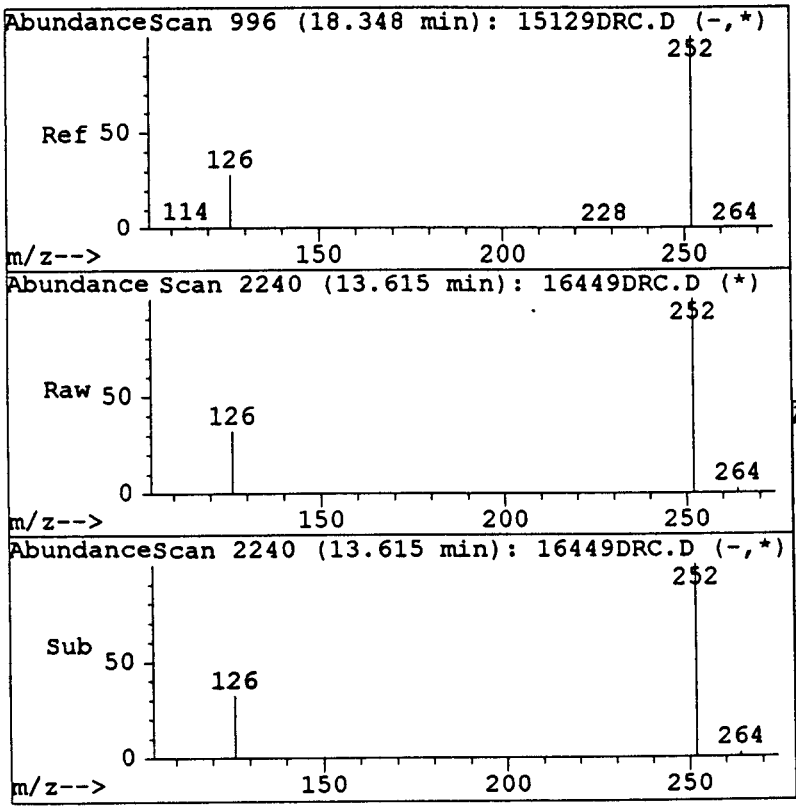


#18
Benzo(e)pyrene
Concen: 337.11 ng
RT: 13.54 min Scan# 2219
Delta R.T. -0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:252 Resp: 69063

Ion	Ratio	Lower	Upper
252	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#19
Benzo(a)pyrene
Concen: 398.13 ng
RT: 13.62 min Scan# 2240
Delta R.T. -0.01 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:252 Resp: 63486

Ion	Ratio	Lower	Upper
252	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

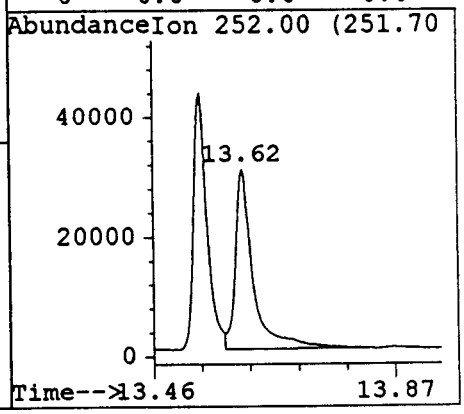
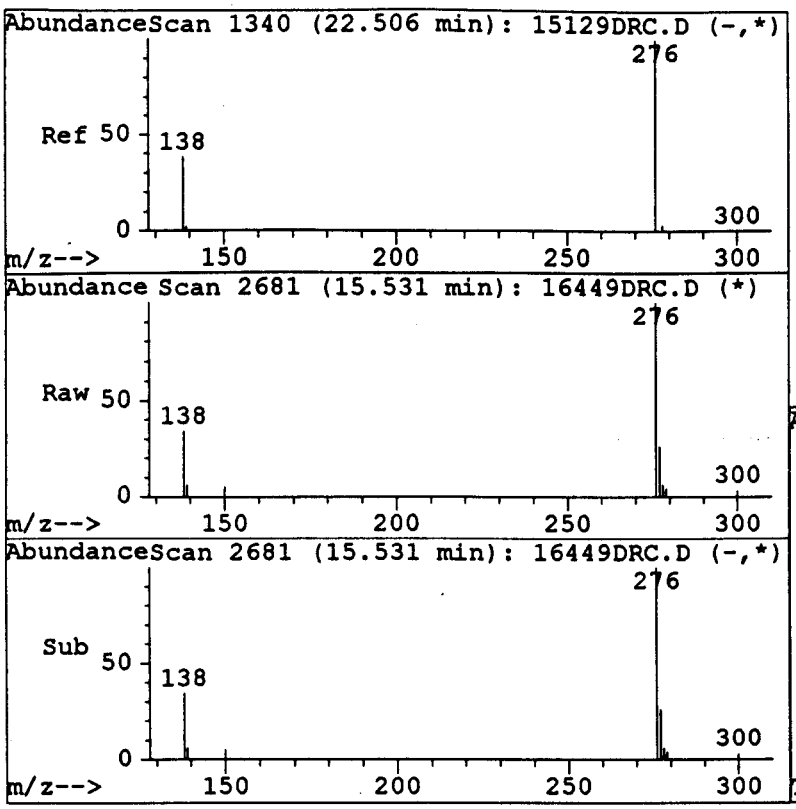


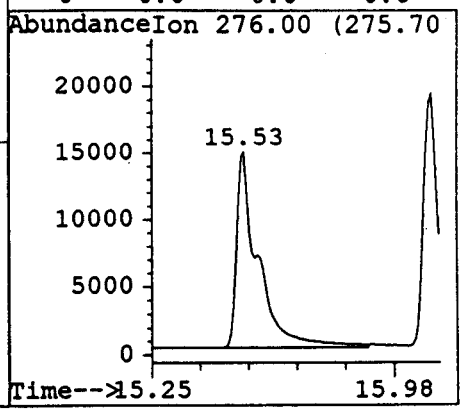
Figure 1g.

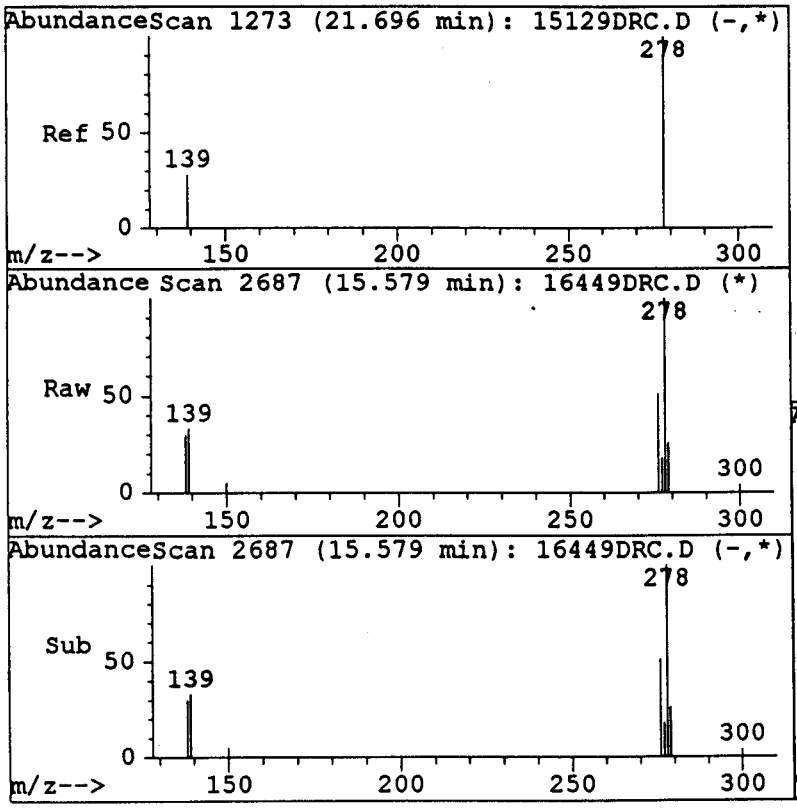


#20
Indeno(1,2,3-cd)pyrene
Concen: 615.39 ng
RT: 15.53 min Scan# 2681
Delta R.T. 0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:276 Resp: 66114

Ion	Ratio	Lower	Upper
276	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#21
Dibenzo(a,h)anthracene
Concen: 464.76 ng
RT: 15.58 min Scan# 2687
Delta R.T. -0.01 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:278 Resp: 47193

Ion	Ratio	Lower	Upper
278	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

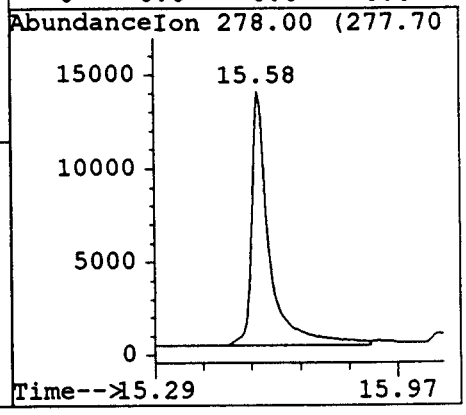
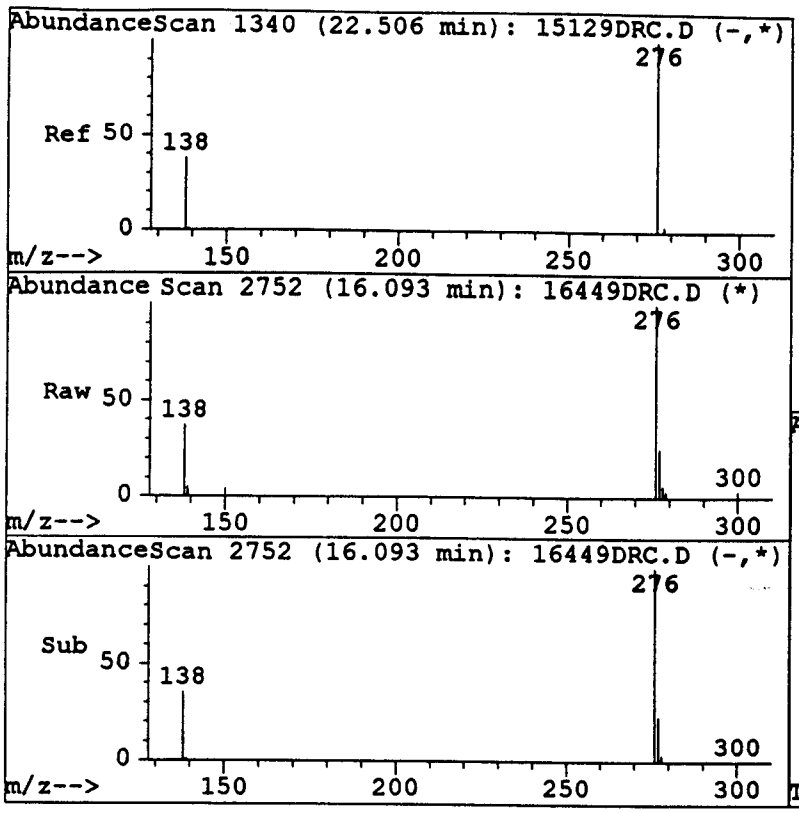


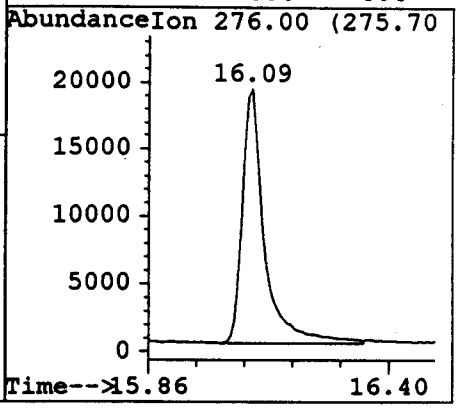
Figure 1h.

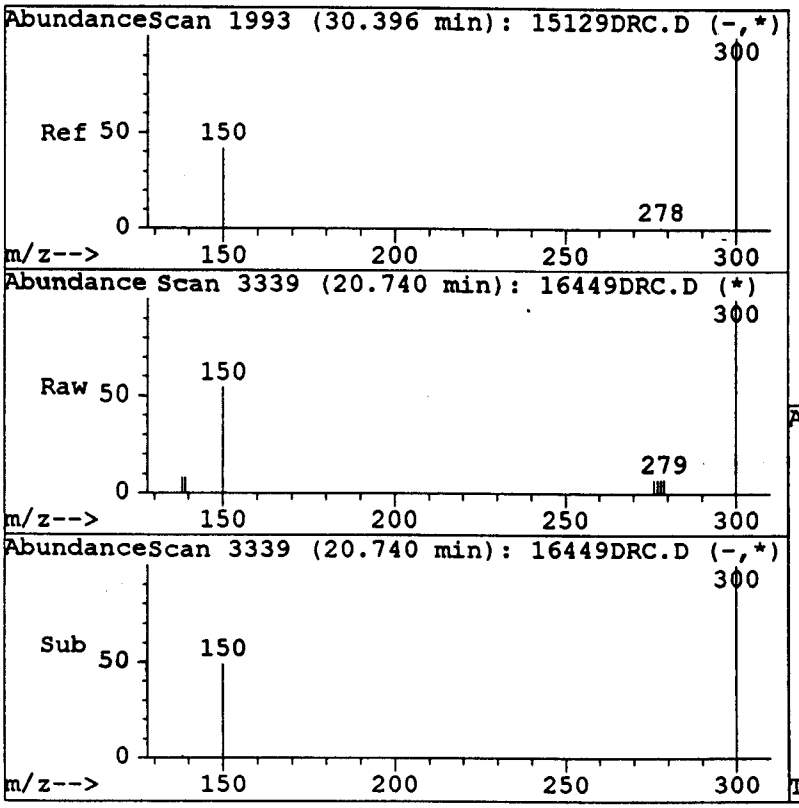


#22
Benzo(g,h,i)perylene
Concen: 363.31 ng
RT: 16.09 min Scan# 2752
Delta R.T. 0.00 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:276 Resp: 64079

Ion	Ratio	Lower	Upper
276	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0





#23
Coronene
Concen: 328.96 ng
RT: 20.74 min Scan# 3339
Delta R.T. -0.01 min
Lab File: 16449DRC.D
Acq: Mon Aug 05 96 12:03:10 PM

Tgt Ion:300 Resp: 44543

Ion	Ratio	Lower	Upper
300	100		
0	0.0	0.0	0.0
0	0.0	0.0	0.0
0	0.0	0.0	0.0

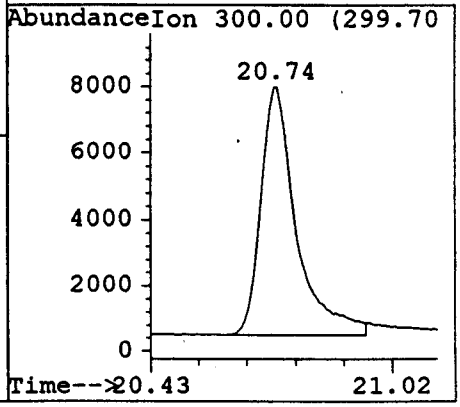


Figure 1i.

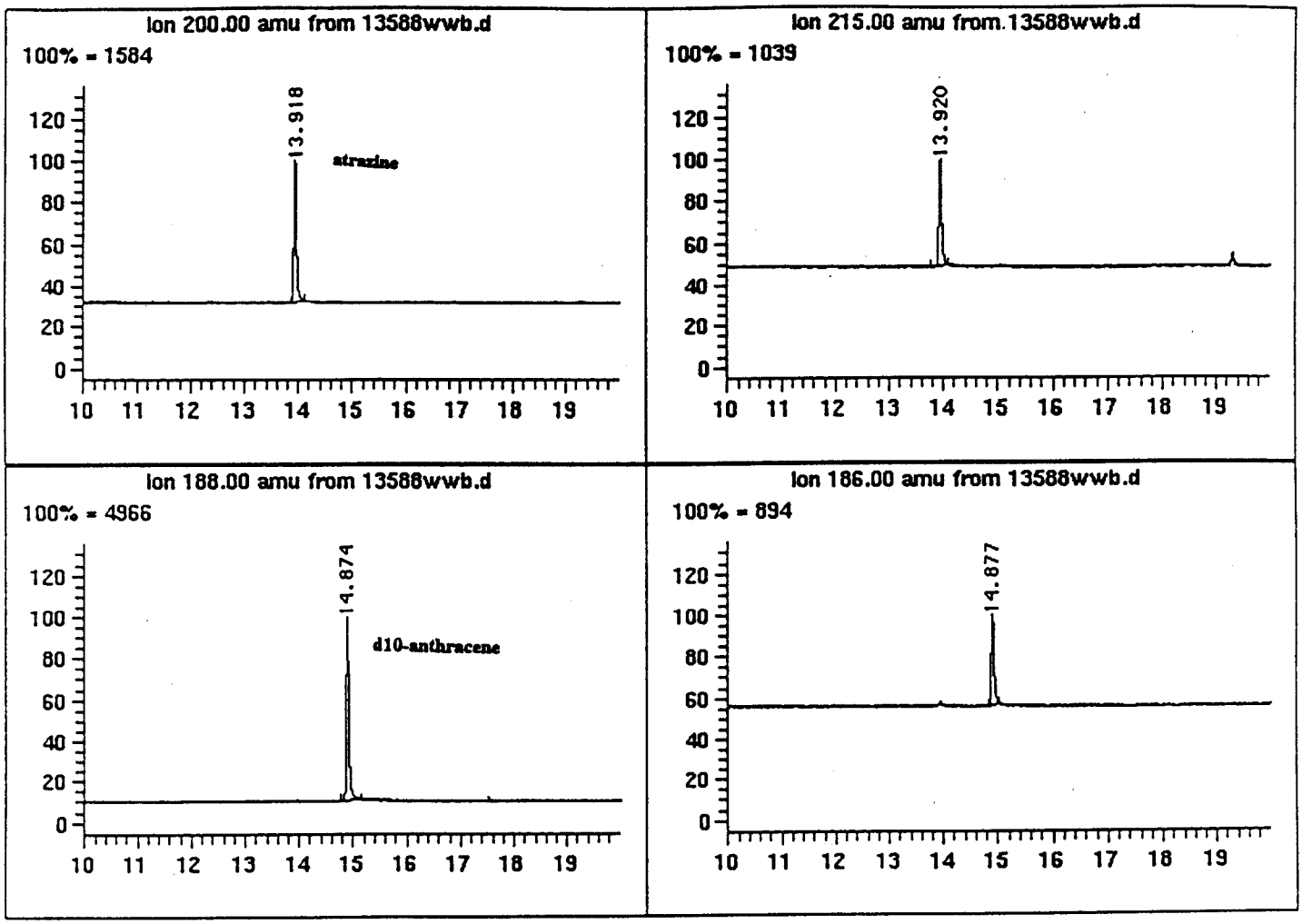


Figure 2. Mass chromatograms for atrazine calibration standard.